Chemical Selection Planning

Screening of four pesticides for possible future biomonitoring

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Presentation to Scientific Guidance Panel
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Purpose of agenda item

- Review preliminary screen on four pesticides in CDPR* Top 100 list
  - Glufosinate ammonium
  - Glyphosate
  - Imidacloprid
  - Propanil
- Obtain Panel input on these as possible candidates for future consideration

*California Department of Pesticide Regulation

Background

- Screening of pesticides as possible candidates for biomonitoring requested by:
  - Scientific Guidance Panel
  - State staff
  - Public

Selection of pesticides for screening

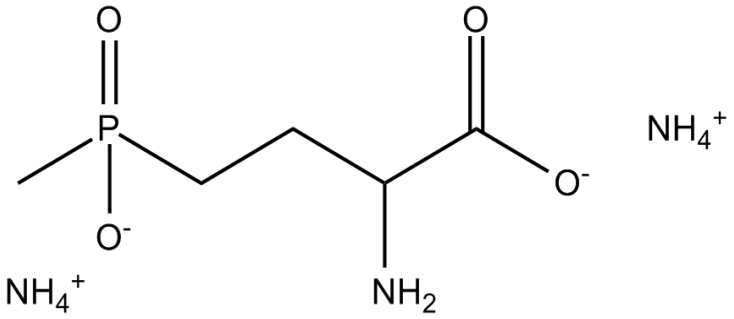
- Volume of use
- Marked increase in use
- Residential/consumer uses

Screen briefly summarizes:

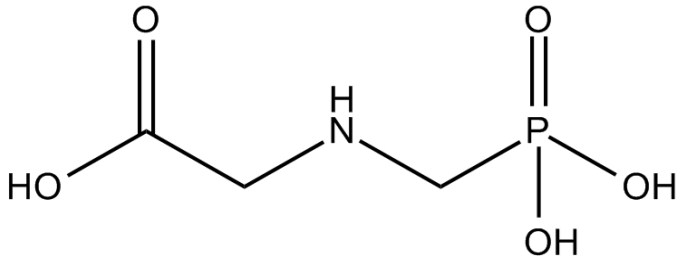
- Exposure sources
- Physical chemical properties
- Persistence and bioaccumulation
- Possible toxicity endpoints
- Key pharmacokinetic factors
- Past biomonitoring studies

Chemical Structures

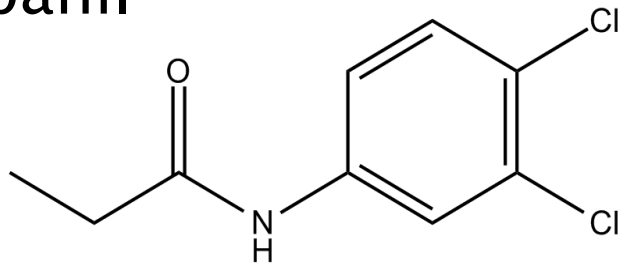
Glufosinate ammonium



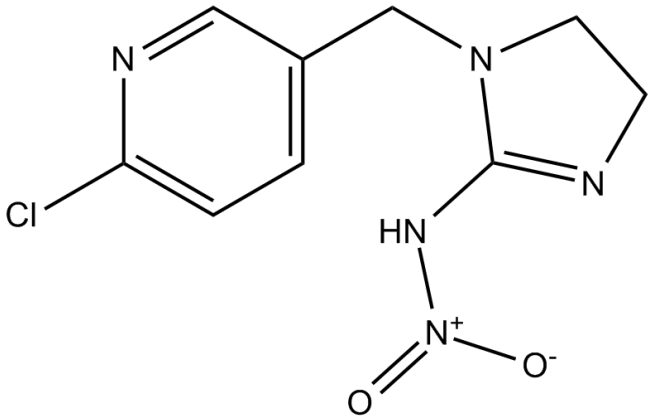
Glyphosate



Propanil



Imidacloprid



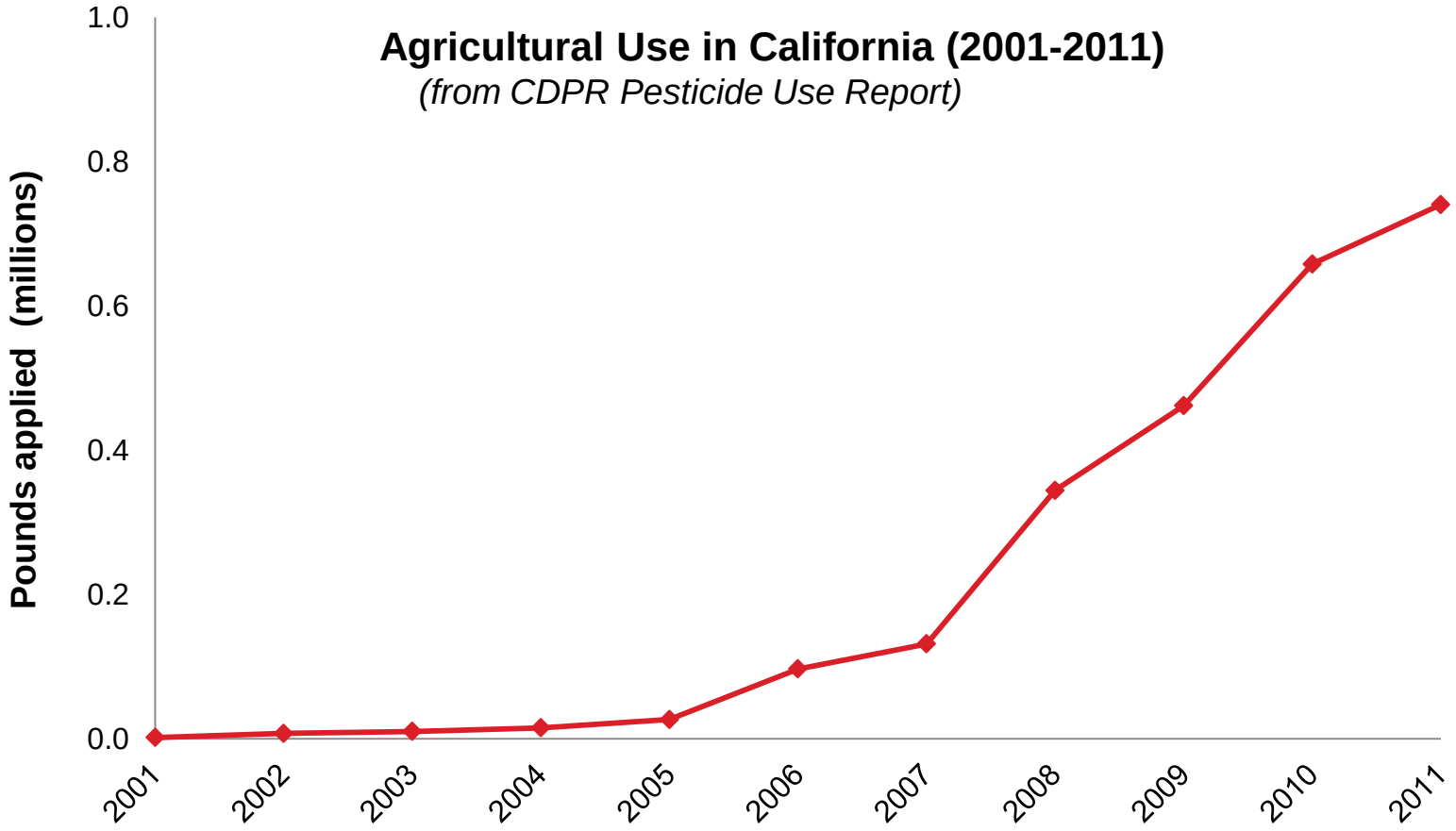
Types of pesticides and uses

Pesticides	Pesticide type and uses
Glufosinate ammonium	Herbicide; crop dessicant Example crops: Corn, almonds, grapes, walnuts Other: Rights-of-way, spot treatments on recreational fields and residential lawns
Glyphosate	Herbicide; plant growth regulator Example crops: Corn, soybeans, almonds, grapes, cotton, pistachios, walnuts, oranges Other: Rights-of-way, landscape and residential gardens

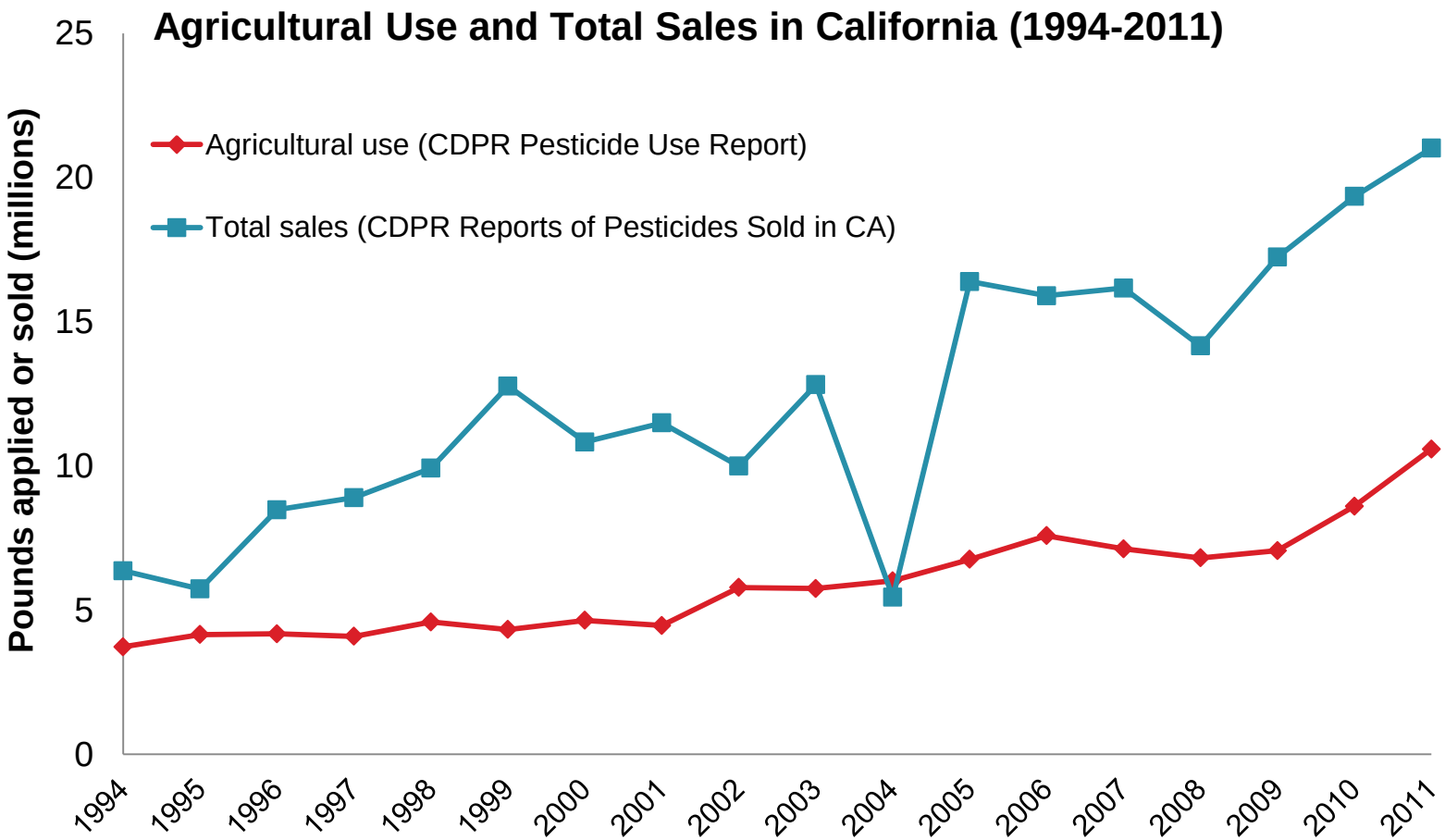
Types of pesticides and uses

Pesticides	Pesticide type and uses
Imidacloprid	Insecticide Example crops: Grapes, oranges, lettuce, tomatoes, broccoli Other: Structural pest control; landscape, lawn, ornamental plant maintenance; pet pesticide; invasive species control
Propanil	Herbicide Crop: Rice

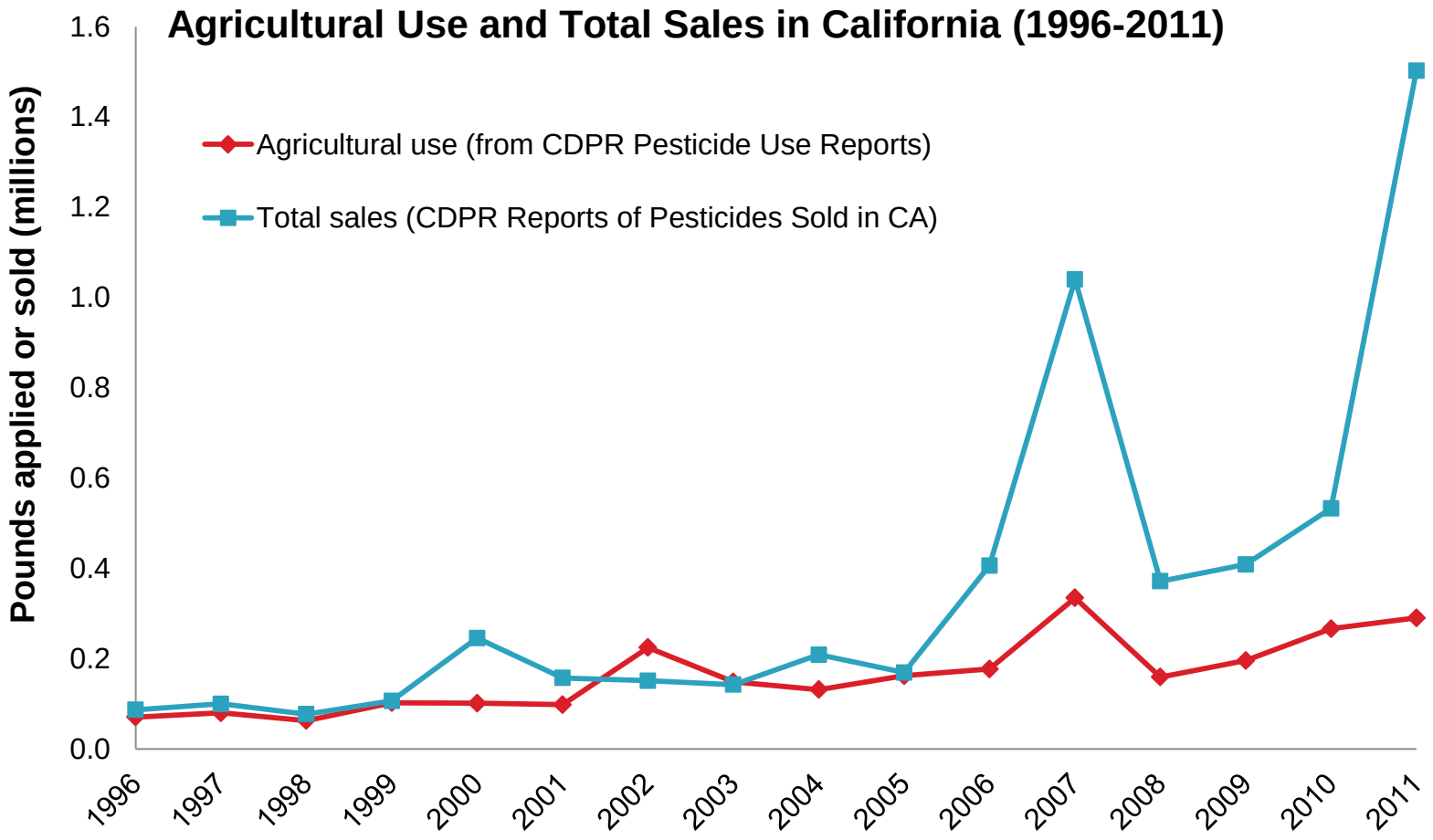
Glufosinate Ammonium



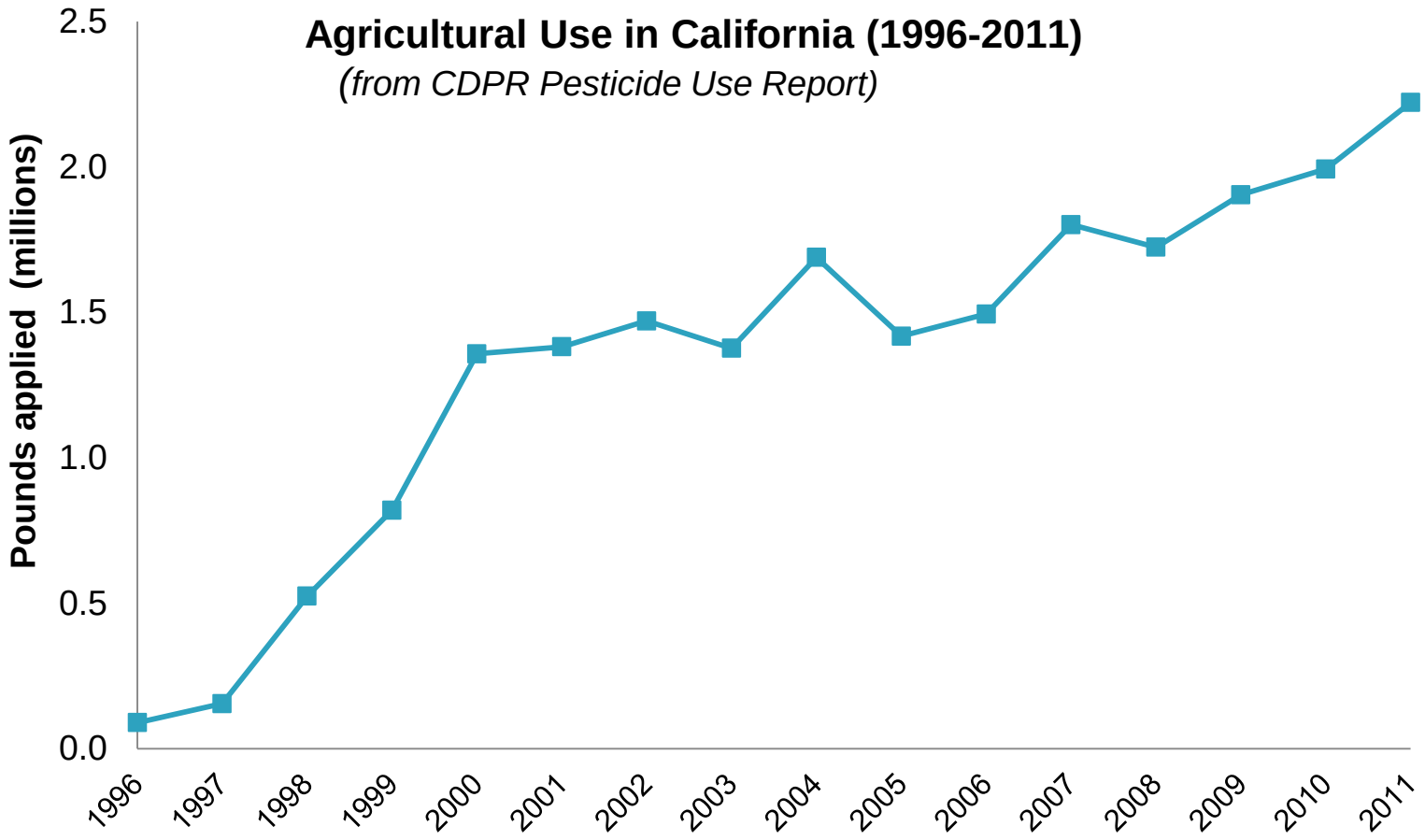
Glyphosate


Agricultural Use and Total Sales in California (1994-2011)
Pounds applied or sold (millions)
25
20
15
10
5
0
Agricultural use (CDPR Pesticide Use Report)
Total sales (CDPR Reports of Pesticides Sold in CA)
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011

Imidacloprid



Propanil


Agricultural Use in California (1996-2011)
(from CDPR Pesticide Use Report)
Pounds applied (millions)
2.5
2.0
1.5
1.0
0.5
0.0
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011

Persistence & bioaccumulation

Chemical	Persistence (P) Bioaccumulation (B)	
	P* US EPA	B** Log K_{ow}
Glufosinate	—	-3.9
3-MPPA*** (3-Methylphosphinicopropionic acid)	—	-0.8
Glyphosate	—	-5.4
AMPA*** (Aminomethylphosphonic acid)	—	-2.1
Imidacloprid	P	0.57
Propanil	P	3.07
3,4-DCA*** (3,4-Dichloroaniline)	P	2.69

* Conclusions of PBT Profiler (US EPA screening tool)
** Log $K_{ow} \geq 4$ considered evidence of possible bioaccumulation
*** Metabolite and/or environmental degradate

Potential exposure sources

- Type of information:
  - Residues in food
  - Exposures from residential use
  - Detections in the outdoor environment

Residue data (produce, crops)

Chemical	Residue data located
Glufosinate	No crop/produce residue data located from US monitoring programs
Glyphosate	USDA produce monitoring (2010-2011) – US soybeans Detected in 271/300 samples. Range: 0.26-18.5 ppm AMPA detected in 287/300 samples. Range: 0.26-20 ppm

Residue data (produce, crops)

Chemical	Residue data located
Imidacloprid	CDPR produce monitoring (2011) Range: 0.012–0.516 ppm USDA produce monitoring (2011) Percent detects: cherry tomatoes, 20%; lettuce, 36%; sweet bell peppers, 26%
Propanil (or 3,4-DCA)	US EPA (2007) – Studies cited in modifying tolerances Reported range of 0.03–8.7 ppm, but not in polished rice FDA (2008) pesticide monitoring: Reported in list of pesticides "detectable and found" USDA (2009) produce monitoring: 1 detection in 435 rice samples

House dust: Glyphosate

Type of household	Detection frequency	Residue in dust Adjusted geo mean* (ng/g dust)
Non-farm (6 homes; 33 samples)	85%	110
Farm (5 homes; 31samples)	100%	
No spray		1000
Spray within 7 days		1300

*See Curwin et al. (2005) for details

Imidacloprid exposure from pet pesticide use

- Six dogs treated with Advantage® (9.1% imidacloprid)
- Transfer from dogs' coats to cotton glove, through 4 weeks

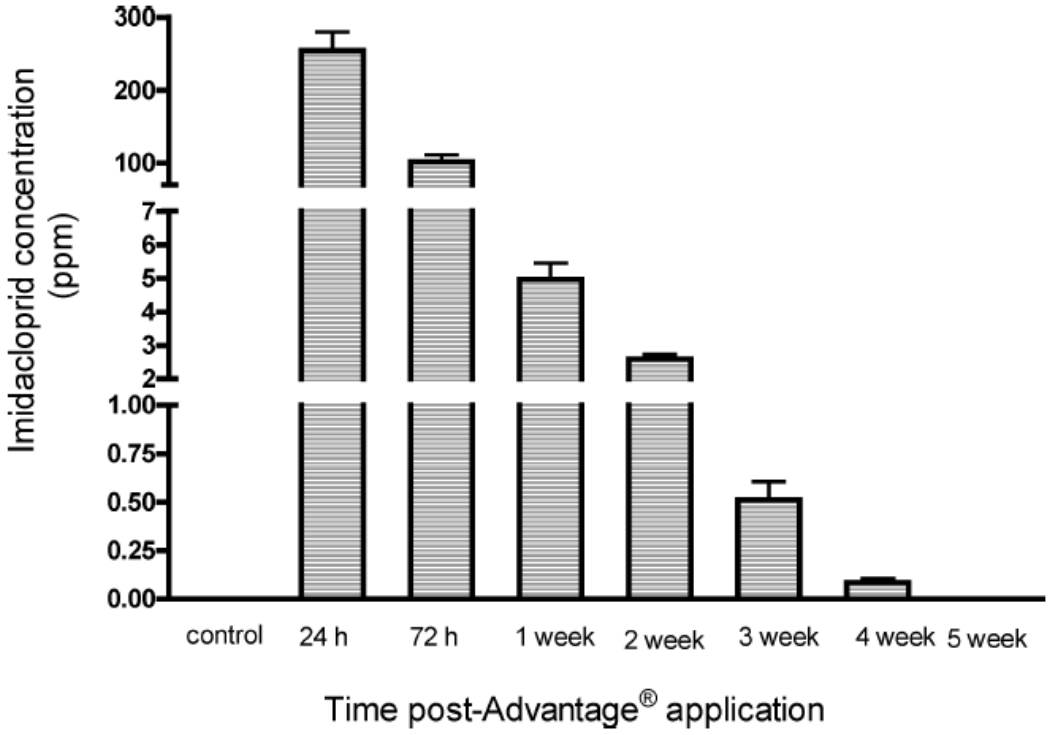


Figure from Craig et al. (2005)

Detections in outdoor environment

Chemical	Environmental media
Glufosinate	Detected infrequently in monitoring of US surface water and groundwater Not detected in California
Glyphosate	Some US surface water and groundwater samples (AMPA also detected) Surface water in some California counties
Imidacloprid	Surface water in some California counties
Propanil (or 3,4-DCA)	Ambient air, surface water and ground water in some California counties

Ability to biomonitor

- Extent of absorption?
- Rate of elimination and by what route (e.g., urine or feces)?
- Is there a biomarker that is specific for the chemical?
- Is there an analytical method?
- Has the chemical been found in humans?

Pharmacokinetic factors

Chemical	Pharmacokinetic factors (studies in laboratory animals)	
	Absorption (oral)	Excretion rate (primary route)
Glufosinate	5–10%	Rapid (feces)
Glyphosate	30–36%	Rapid (feces, urine)
Imidacloprid	>90%	Rapid (urine)
Propanil (3,4-DCA)	Rapid	Rapid (urine)

Human biomonitoring studies

Chemical	Detected in*
Glufosinate	Serum
Glyphosate	Urine
Imidacloprid	----
Propanil (3,4-DCA)	Urine

**Studies of non-occupationally exposed individuals*

Preliminary screen summary

Chemical	Use Increasing (↑) Residential (✓)	Predicted to be Persistent	Detected in			Other notes
			Crops/ produce	House dust	Humans	
Glufosinate ammonium	↑				✓	EU phase-out
Glyphosate	↑ ✓		✓	✓	✓	
Imidacloprid	↑ ✓	✓	✓			
Propanil	↑	✓	✓		✓	EU phase-out

Options for the Panel

The Panel can recommend that the Program:

- Gather additional screening information on any of these pesticides
- Prepare document(s) to support consideration of one or more of these pesticides as potential designated chemicals
- Continue tracking these pesticides
- Not consider these pesticides further

Other chemical selection activities

- Potential designated chemicals:
  - Synthetic musks
  - Organotins
- Additional metals that EHL can measure as potential designated/priority chemicals
- Continuing to track possible target analyte(s) for diesel exhaust